Abiotic persistence of atrazine and simazine in water

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Abstract: Hydrolysis and photolysis experiments have been undertaken to investigate the abiotic persistence of atrazine and simazine in a variety of waters. Hydrolysis only occurs to a significant extent at pH values at the lower limit of those found in the natural aquatic environment (pH 4.0 or less). Photolysis was initiated by a wide range of wavelengths in waters at pH 4.0, but only by more energetic wavelengths of less than 300 nm at higher pH values (pH 6 to 8). Based on these data, the aquatic half-life of atrazine and simazine in well-lit acidic upland waters will be typically six days. In lowland rivers with higher pH (7 to 8.5), these triazines are likely to exhibit half-lives of months rather than days. In groundwaters, atrazine and simazine will have half-lives in the order of years, due to the exceedingly slow rate of hydrolysis.

Keywords: atrazine; simazine; abiotic; persistence; hydrolysis; photolysis; river water.

1 INTRODUCTION

Atrazine and simazine were very popular chlorotriazine pesticides used in the UK as systemic herbicides for the control of pre-emergent weeds in cereals and for total vegetation control on banks and railways. Their agricultural use is now restricted to maize (atrazine and simazine), beans, pome fruits, hops, vegetables, ornamentals and other crops (simazine) and to rates not exceeding 1.5 kg AI ha^{-1}. Their persistence and solubility, however, ensure they are still of concern in the aquatic environment. A recent report, for example, states that atrazine is found to exceed the Drinking Water Limit of 0.1 μg $litre^{-1}$ in groundwater in over 10% of the samples collected.[1]

Atrazine and simazine can be detected in the majority of surface water and ground waters of lowland areas where intensive agriculture is practised, particularly where land has been given over to maize cultivation.[2,3] Concentrations in surface water and groundwaters, when detected, are usually around 100 ng $litre^{-1}$ or less, although levels over 1 μg $litre^{-1}$ have been reported.[3,4]

In studies using river water, a half-life of approximately one month for atrazine has been measured.[5] A considerably longer half-life of five months was estimated for atrazine added to lake enclosures,[6] and microcosm experimental data appear to vary considerably depending on conditions (half-life 3–12 days for estuarine microcosms;[7] *c* 80 days for laboratory microcosm).[8] Other workers have also measured the half-life of atrazine to be in the order of four to eight months in small ponds.[9,10] Similar half-lives (nine months) were obtained for simazine in a lake study in America.[11]

Degradation has been shown to be enhanced in the presence of H^+ ions,[12] either via humic and fulvic acids present dissolved in the water[13] or by surface-catalysed hydrolysis after sorption to particles.[5] Hydrolysis is likely to be initiated by the COOH plus phenolic and/or enolic OH functional groups present on these compounds.[14] Increasing dissolved fulvic acid concentration from 500 to 5000 mg $litre^{-1}$ in atrazine-spiked water incubated in the dark reduced the half-life for atrazine in solution from 742 to 287 days at pH 7 (25 °C) and from 34.8 to 4.6 days at pH 2.9.[13] It was not stated whether or not the samples had been sterilised.

Photolysis experiments have included irradiation in sunlight,[15] at 254 nm using a mercury lamp[16,17] and at greater than 340 nm using a xenon lamp, to mimic natural radiation more closely.[18–20] Most of the experiments carried out using high-intensity, low-wavelength light were designed to assess the degradation of atrazine during drinking water treatment, and thus give little insight into the persistence of triazines in the aquatic environment. Other papers using simulated natural light at natural pH have added photo-sensitisers such as titanium oxide or aluminium oxide to catalyse hydrolysis at an unnatural temperature of 60 °C.[19] The effect of humics and fulvics on the indirect photolysis of triazines through photo-sensitisation has also not been particularly well studied. Although these compounds have been shown to

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catalyse hydrolysis in the dark, their effect in the light might differ through quenching of the incident radiation by the functional groups attached to the large-molecular-weight organic compounds. As a result there is a distinct lack of data on the persistence of triazines in a natural aquatic environment.

The persistence of these compounds makes it important to be able to predict their likely persistence under a wide variety of environmental conditions. Previous studies have also rarely attempted to differentiate between the abiotic and biotic processes, resulting in half-lives being calculated for a combination of biotic and abiotic degradation. To obtain a thorough understanding of the aquatic fate of atrazine and simazine, it is essential to obtain specific process data. This paper concentrates on the abiotic degradation of atrazine and simazine under varying conditions of pH (both natural and buffered), and dissolved organic carbon likely to be encountered in the aquatic environment, in natural light, artificial daylight and in the dark.

2 METHODS

2.1 General

Atrazine and simazine concentrations in the aqueous samples were determined directly using a Spectra Physics SP8700XR High Performance Liquid Chromatograph, SP8480XR UV-vis detector and SP4290 integrator. The eluant comprised a ratio of 51:49 acetonitrile (Rathburn HPLC Grade) and double distilled water, degassed with helium. Eluant flow rate was set at 1 ml min^{-1}, and a 50 µl injection loop was used. Atrazine and simazine were detected at a wavelength of 223 nm. A calibration of up to 50 µg $litre^{-1}$ was run at the beginning and end of each batch of samples along with an appropriate analytical quality control sample (Aquacheck, WRc plc). All determinations were made in triplicate, with half-lives being calculated based on first- or second-order reactions, depending on which provided the best fit to experimental data.

Experiments were carried out in methanol-rinsed Pyrex (50 ml) or quartz (20 ml) stoppered tubes. Artificial daylight experiments were conducted in a constant light and temperature incubator, lit with fluorescent tubes for 16 h a day at a temperature of 25 °C, with an intensity of 7000 lux. The fluorescent tubes emitted light between 300 and 400 nm with a broad maximum at *c* 350 nm. Duplicate studies were carried out using both Pyrex and quartz vials. Unlike quartz, Pyrex absorbs light below 300 nm, thus allowing a measure of the significance of the more energetic sub-300 nm radiation in the photolysis of atrazine and simazine.

All samples were initially spiked with 50 µg $litre^{-1}$ atrazine and simazine from a stock standard (10 mg $litre^{-1}$) made up in methanol. Tests showed that there was no significant adsorption of atrazine to the glassware walls.

Where experiments were required to be conducted under sterile conditions, all glassware, buffers, double-distilled water and river waters were autoclaved prior to the start of the experiment. Natural water samples were collected from the river Thames (lowland hard water, pH 8.2) in Southern England, the river Goyt (upland soft water, pH 4.5) in Derbyshire England and Burbage Brook (upland soft water, pH 6.4) in Yorkshire. All river waters were filtered to 0.4 µm using Nuclepore polycarbonate membranes, and stored in the dark prior to use in experiments.

2.2 Hydrolysis

Hydrolysis experiments were conducted in the dark at 15 °C to measure pure abiotic hydrolysis rates using the following pH values and buffers:

(i) pH 4.0 – 0.1 M sodium citrate in distilled water (DW)
(ii) pH 6.8 – 0.025 M potassium dihydrogen phosphate/0.025 M disodium hydrogen orthophosphate in DW
(iii) pH 9.0 – 0.05 M sodium tetraborate in DW
(iv) pH 8.2 – Thames river water filtered and unbuffered.

In order to assess whether the rate of pure hydrolysis could be influenced by surface-catalysed hydrolysis, iron hydroxide and aluminium silicate were spiked into deionised water containing atrazine and simazine under sterilised conditions (by autoclaving). The samples were kept in the dark and shaken daily to keep the solids in suspension. The pH of these solutions remained at *c* 8.0 for the duration of the incubations. The experimental conditions are listed in Table 1.

2.3 Photolysis

In order to assess the significance of sunlight on the persistence of atrazine and simazine in water, experiments were conducted both in river waters of varying pH and DOC (Table 2), and also with buffered samples in artificial light and daylight.

Table 1. Experimental conditions for abiotic hydrolysis studies of atrazine and simazine

pH			
4.0	7.0	8.0	9.0
DW[a]	DW	Thames (sterilised)	DW
		Thames (non-sterilised)	
		DW + Fe (hydroxide)	
		DW + Al (silicate)	

[a] DW = Distilled water.

Table 2. River waters used for hydrolysis/photolysis experiments

Water	*pH*	*DOC (mg $litre^{-1}$)*
Lowland (high pH)	8.20	5.0
Upland (high DOC)	6.41	10.0
Upland (low pH)	4.50	1.7

	pH			
(*Buffered DW*)		(*River waters*)		
4.0	7.0	4.5	6.4	8.2
Daylight[a]				
DW[b] (quartz)	DW (quartz)			
DW (glass)	DW (glass)			
Artificial light				
DW (quartz)	DW (quartz)	RW[c] (quartz)	RW (quartz)	RW (quartz)
DW (glass)	DW (glass)			

[a] Spiked (50 μg litre^{-1}) DW (buffered at pH 4 and 7), exposed to natural light in Pyrex and quartz vessels over a period of approximately one month (August).
[b] DW = Distilled water.
[c] RW = River water.

Table 3. Experimental conditions for abiotic photolysis of atrazine and simazine

The upland low pH water was shown to be unstable during photolysis, with the pH drifting from 4.4 to 6.2 during the course of the experiment (probably due to the photolytic degradation of the humic and fulvic acids). A second photolysis experiment was therefore conducted with the addition of citrate buffer (40 g litre^{-1}; pH 4.0) to stabilise the pH at 4.5 for the duration of the incubation.

The studies conducted to assess the photolytic behaviour of the herbicides are listed in Table 3.

3 RESULTS AND DISCUSSION

3.1 Atrazine and simazine hydrolysis

No appreciable degradation of atrazine or simazine was observed over a period of 100 days at 15 °C in the dark in pH 7 and pH 9 buffer solutions and Thames River water. This confirmed previous findings that the hydrolysis of atrazine and simazine is negligible in the dark at pH >4, which is the lowest pH that would be expected to be found in the aquatic environment.[21] The estimated half-life of atrazine in neutral, sterile water, for example, is 1800 years.[22] This therefore suggests that, in groundwater, the persistence of atrazine and simazine is likely to be measured in years rather than days, particularly as the influence of biotic degradation will be less. Experiments have shown negligible degradation of atrazine in two subsurface environments (one near a road where atrazine had been applied for 12 years, and the other where atrazine had not been applied), after 160 days.[23]

Humic and fulvic acids have been shown to catalyse the hydrolysis of triazines in water. The hydrolysis half-life of atrazine has been shown to be reduced to only 4.6 days,[13] but fulvic acids were present at 5000 mg litre^{-1}, (pH 2.4, 25 °C), which is three orders of magnitude greater than found in the environment. Reducing the fulvic acid concentration to 500 mg litre^{-1} (pH 7.0, 25 °C), increased the half-life to 742 days, which is still much shorter than that calculated for pure water at pH 7.0 (1800 years), and therefore suggests that humics and fulvics may provide a catalytic effect, but one that would only be detectable over the course of years rather than days.

A similar lack of degradation was observed for the solutions containing iron and aluminium. It has previously been shown that the rate of hydrolysis of triazines in aqueous solutions is increased by the addition of soil,[24] and it was suggested that iron and aluminium contained in minerals in the soil catalysed the hydrolysis by behaving like Lewis-type acids.[25] Our data, however, do not support this proposed mechanism, but the experiments were performed in the dark, and it is therefore possible that light is required to initiate the hydrolysis reaction via the production of radicals.

There was, however, slow degradation of both atrazine and simazine in buffered samples at pH 4.0 (Figs 1a and b). Simazine concentrations decreased from *c*42 μg litre^{-1} to 25 μg litre^{-1} over the period of incubation, approximating to a half-life of 145 days. Slower degradation was recorded for atrazine at pH 4, with concentrations decreasing from *c*50 to 34 μg litre^{-1} over 100 days, with a calculated half-life of 225 days.

3.2 Atrazine and simazine photolysis/hydrolysis

3.2.1 Buffer solution incubations

3.2.1.1 Artificial light. The combined rate of photolysis and hydrolysis of the two herbicides in experiments carried out under artificial light using quartz vessels was similar at both pH 4 and pH 7 (Figs 2a and b, 3a and b), approximating to a first-order decay for atrazine with calculated half-lives of 17 and 19 days respectively (Table 4). The degradation of simazine was found to best fit a second-order decay, with half-lives for pH 4 and pH 7 being calculated as 21 and 19 days respectively (Table 4). Decomposition was slower in the Pyrex tubes, with both simazine and atrazine exhibiting close approximations to first-order rate reactions. At pH 4 (Figs 4a and b) the half-lives for the photolysis of atrazine and simazine were 34 and 32 days respectively (Table 4), almost twice that in the quartz vessels, but still significantly faster than that recorded for solely hydrolytic degradation in the dark. At pH 7 and in Pyrex incubation vessels atrazine had a half life of *c*155 days (Figs 5a and b), whilst the half life for simazine was measured at *c*160 days.

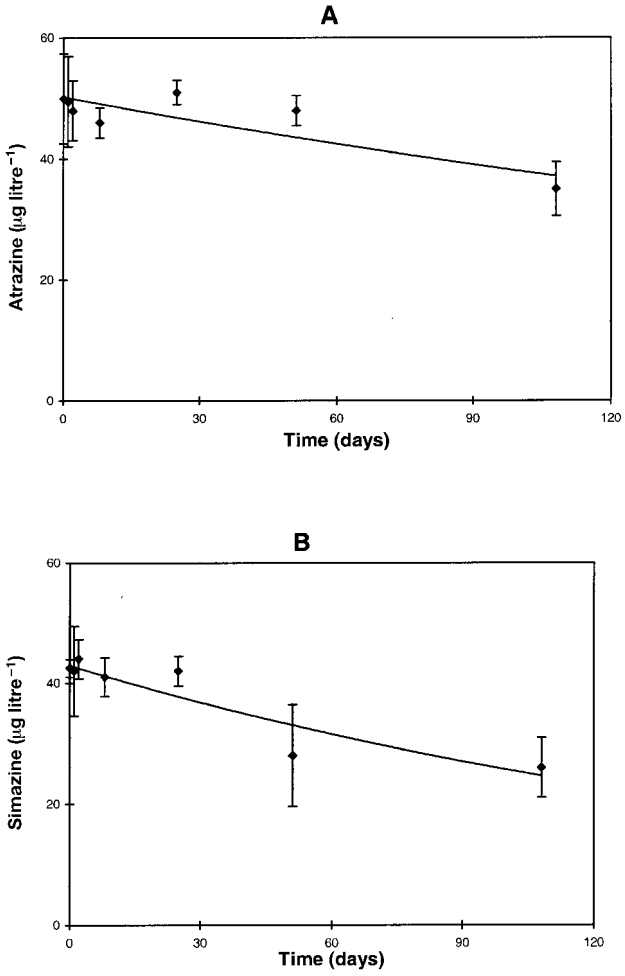

Figure 1. Hydrolysis of (A) atrazine and (B) simazine in dark at pH 4.0 (error bars are 95% confidence intervals).

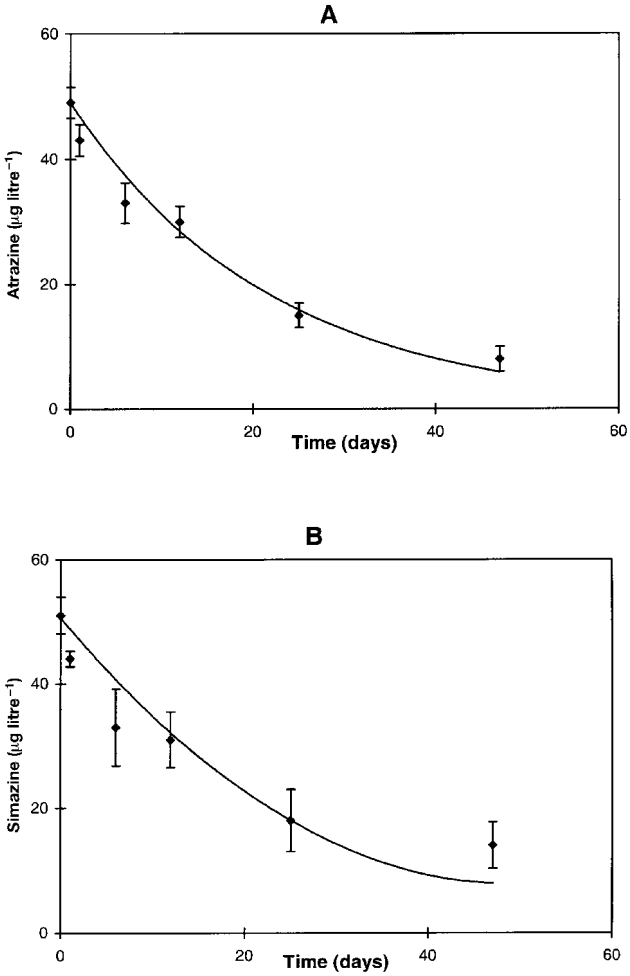

Figure 2. Photolysis/hydrolysis of (A) atrazine and (B) simazine in quartz vessels at pH 4.0 under artificial light (error bars are 95% confidence intervals).

The fact that half-lives for both atrazine and simazine were significantly less for samples exposed in quartz tubes compared with identical ones in Pyrex vessels (300 nm cut-off), suggests that, at environmentally realistic conditions with water at around pH 7.0, in the absence of any photo-sensitisers, photolysis is mainly initiated by light with wavelengths of less than 300 nm.

3.2.1.2 Daylight. Spiked samples exposed to solar radiation with a midday intensity approximately 10 times that of the artificial light for a sunny day (which accounted for 70% of the exposure period), exhibited an expected shorter half-life of degradation of between six and 10 days for both Pyrex and quartz vessels for the triazines at pH 4.0 (Table 4). At pH 7.0, however, the samples in the Pyrex tubes displayed no significant degradation, whereas the samples contained in the quartz vessels decomposed to give a calculated half-life of 18 days for atrazine and 37 days for simazine. It therefore appears that, at pH 4, the solar radiation was sufficiently intense to initiate the hydrolysis successfully even in the Pyrex tubes, but at pH 7.0 the activation energy of hydrolysis could not be exceeded.

There are few literature data with which to compare directly these results, because previous studies involving photolysis have generally irradiated samples with sub-300-nm light in order to decompose triazines for water purification purposes. Often, photo-sensitising compounds such as titanium oxide, iron hydroxides or organic solvents have been added in order to promote indirect photolysis. Rates of hydrolysis are very much dependent on the energy and intensity of the radiation. For example, irradiation of atrazine at 254 nm using a low-pressure mercury lamp, in combination with ozonation, reduced the half-life to a matter of minutes, even at atrazine concentrations of 1000 mg litre^{-1}.[17] Using simulated solar radiation to expose simazine and atrazine in an aqueous suspension of titanium oxide particles, the half-life of atrazine was again shortened to only a few minutes.[19] Conversely, the half-life for the photo-reaction of atrazine with hydroxy radicals in clean water was calculated as 340 days for light above 290 nm.[26]

Under more environmentally realistic conditions, the exposure to sunlight (mean 9.1 h per day) of aqueous solutions of atrazine resulted in a half-life of 2.6 days,[27] with decomposition products including hydroxyatrazine (14.6%), de-ethylated atrazine

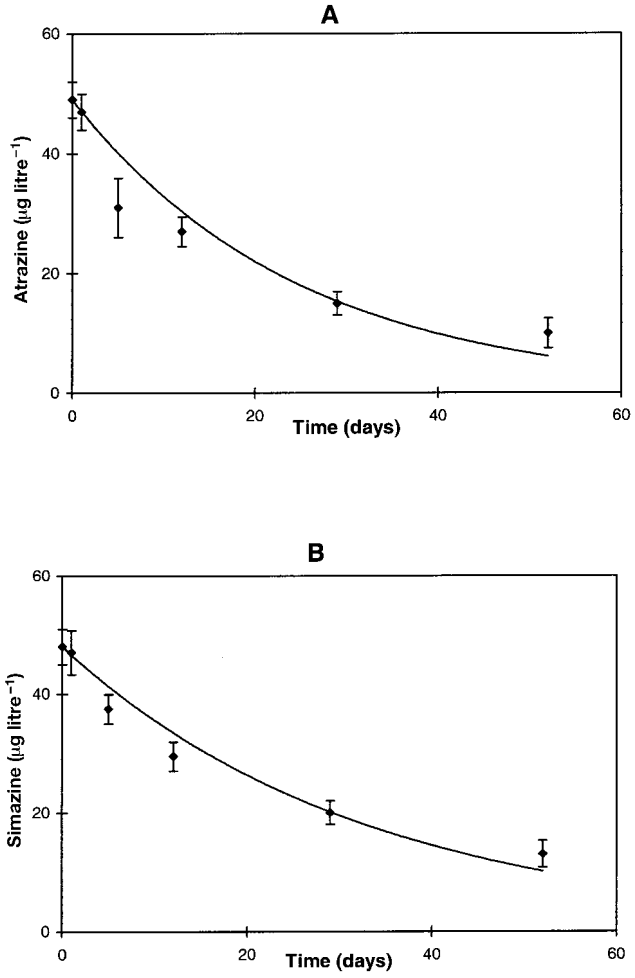

Figure 3. Photolysis/hydrolysis of (A) atrazine and (B) simazine in quartz vessels at pH 7.0 under artificial light (error bars are 95% confidence intervals).

(38%), de-isopropyl atrazine (4.3%) and de-alkylated atrazine (22%), all of which are less toxic than the parent compound. Unfortunately the pH of the sample and intensity of radiation were not quoted. Experiments using a xenon lamp emitting radiation between 300 and 800 nm (similar to natural solar radiation) to irradiate atrazine in distilled waters showed that atrazine was degraded to hydroxyatrazine (half-life *c*1 h) which persisted.[28]

Given that there is only a small spectral overlap between the UV/VIS-absorption spectrum of simazine and atrazine (λ_{max} = 221 nm)[21] and sunlight (300–800 nm), observed photolysis may be a consequence of poor shielding of radiation below 290 nm under artificial light conditions. The observed photolysis in buffer solutions exposed to natural sunlight as part of this work, however, indicates that although sub-300-nm radiation only makes up a small percentage of the solar spectrum, it is of sufficient intensity to promote photolysis of the triazines. The proportion of abiotic degradation through direct and indirect (through photo-sensitisation) photolysis will therefore be dependent on several factors such as the presence of photo-sensitisers in the water, and sunlight intensity.

Table 4. Kinetic data for photolytic/hydrolytic and hydrolytic degradation of atrazine and simazine

	Half-life (days)	
	Atrazine	*Simazine*
Dark (hydrolysis)		
pH 4	225	145
pH 7	ND[a]	ND
pH 9	ND	ND
Thames water (autoclaved)	ND	ND
Thames water (non-autoclaved)	ND	ND
DW + iron hydroxide	ND	ND
DW + aluminium kaolin)	ND	ND
Artificial light (photolysis/hydrolysis)		
Quartz pH 4	17	21
Pyrex pH 4	34	32
Quartz pH 7	19	19
Pyrex pH 7	155	160
Thames water pH 8.2 (low DOC)	ND	ND
Upland water pH 6.4 (high DOC)	ND	ND
Upland water buffered pH 4.5 (med DOC)	40	35
Daylight (photolysis/hydrolysis)		
Quartz pH 4	6	6
Pyrex pH 4	10	7
Quartz pH 7	18	37
Pyrex pH 7	ND	ND

[a] ND = No significant degradation measured.

3.2.2 *River water incubations*

3.2.2.1 Artificial light. The three river samples offered a good representation of most conditions encountered in the riverine environment, and would therefore highlight any effects natural fluctuations in pH and DOC might have on the persistence of triazines in water. For the two higher pH solutions (pH 8.2, DOC 5.1 mg litre^{-1} and pH 6.4 DOC 10 mg litre^{-1}), no significant degradation was observed over a period of approximately 30 days when incubated in the quartz vessels. This was surprising, as buffered distilled water samples at pH 7 exhibited a half-life in the order of only 10–20 days under the same lighting and temperature conditions. The half-life of the triazines spiked into the low-pH water (weakly buffered to pH 4.5) also increased with respect to those in a pH 4.0 buffer solution, up to 40 days for atrazine and 35 days for simazine from only 16.5 and 21 days respectively. This therefore suggests that, although at very high concentrations humics and fulvics can enhance hydrolysis in the dark,[13] in natural waters (at low mg litre^{-1} concentration) they may actually retard photolysis[29] under certain lighting conditions (artificial incident light in this case). Under natural conditions where the intensity of radiation (in the summer) is at least ten times greater than that provided by the artificial source, quenching by humic substances is likely to be exceeded and the photo-sensitisation properties of ferric ions, suspended oxides and humics will promote degradation.

Unsterile, non-autoclaved samples incubated in the

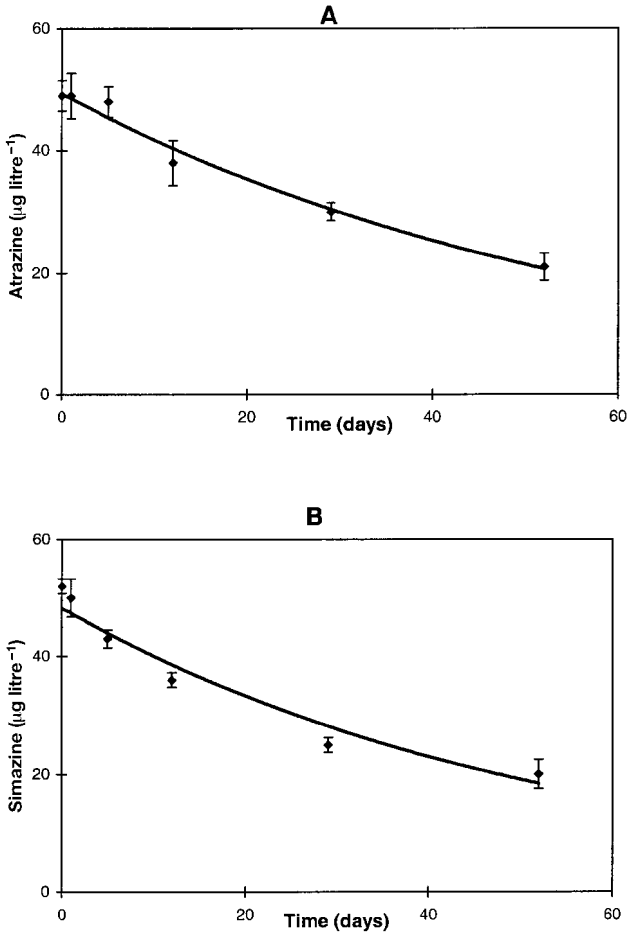

Figure 4. Photolysis/hydrolysis of (A) atrazine and (B) simazine in Pyrex vessels at pH 4.0 under artificial light (error bars are 95% confidence intervals).

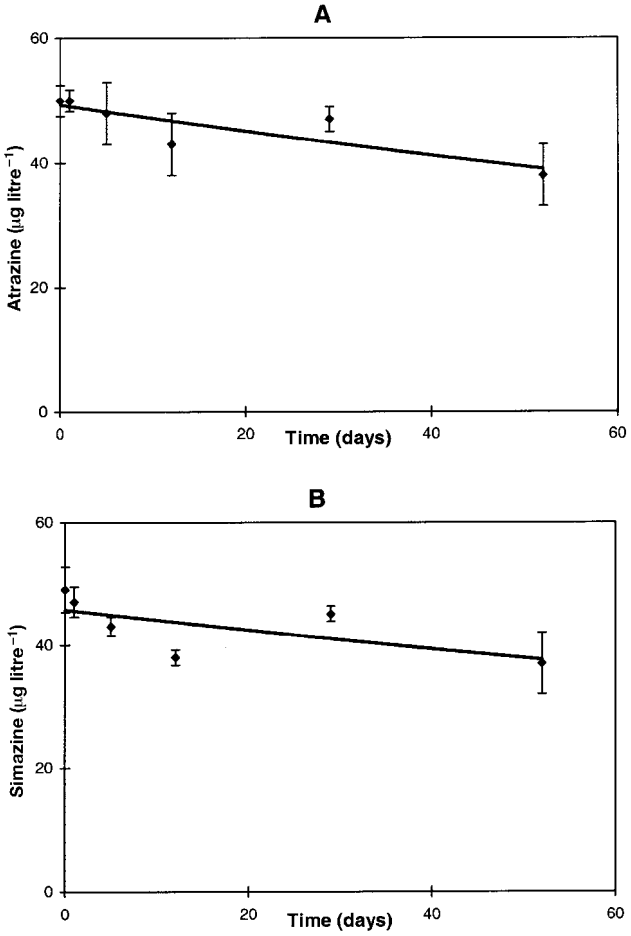

Figure 5. Photolysis/hydrolysis of (A) atrazine and (B) simazine in Pyrex vessels at pH 7.0 under artificial light (error bars are 95% confidence intervals).

dark also failed to result in degradation of the two triazines, even though appreciable microbial growth was observed in the vessels. Previous studies, however, have suggested that, although a wide variety of aquatic algae, bacteria and fungi can degrade triazines (generally by dealkylation),[21,30,31] biodegradation is generally slow,[30] and under certain conditions may not occur at all,[32] which appears to be the case for Thames river microbiota.

4 CONCLUSIONS

In the absence of light, atrazine and simazine exhibit significant abiotic hydrolytic degradation only at or below pH 4 in either buffered solutions or natural waters. The presence of iron and aluminium hydroxides also failed to promote hydrolysis, contrary to some reports. This therefore suggests that significant abiotic degradation will only occur in groundwaters of low pH, found in upland peat-rich waters. The presence of humic and fulvic acids in such waters may also serve to catalyse the hydrolysis, although the half-lives of the triazines will still be measured in years.

For surface waters photolysis can be predicted to occur readily in waters of all pH values (ranging from only about six days at pH 4 to between 18 and 37 days at pH 7.0) and, given the known resistance of triazines to biodegradation, photolysis is likely to be the major degradation pathway in the aquatic environment. Photolysis is likely to occur both through direct photodegradation by high-energy solar radiation, as demonstrated in this work where degradation occurred at pH 7.0 only in vessels that allowed the transmission of sub-300-nm radiation (quartz), and also at longer wavelengths through indirect photo-sensitisation by humics, ferric ions and suspended oxides, as shown by previous workers.

The relative significance of each photolytic pathway will be dependent on a number of environmental parameters, including intensity of sunlight and the concentration of photo-sensitisers present. These factors appear to be particularly important in controlling how humic compounds affect the fate and behaviour of triazines in the aquatic environment. Natural waters containing humics (DOC levels up to 10 mg litre^{-1} for pH 6.4 water), retarded photolysis of simazine and atrazine compared with buffer solutions of the same pH, probably through the humics quenching the low-level artificial light. Previous workers, however, have shown humics and fulvics to

accelerate degradation in the dark through the presence of H^+ ions and to photo-sensitise degradation under certain conditions (eg full sunlight, high concentrations of humic or fulvic acids).

Overall, temporal variations in the rate of photolysis as the intensity of solar radiation changes on a seasonal basis can therefore be expected in natural waters. Simazine and atrazine present in low-pH waters during the summer months will persist for a matter of days, compared with months for triazines in higher pH water during the winter months.

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